



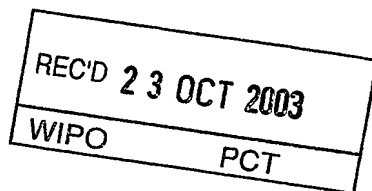
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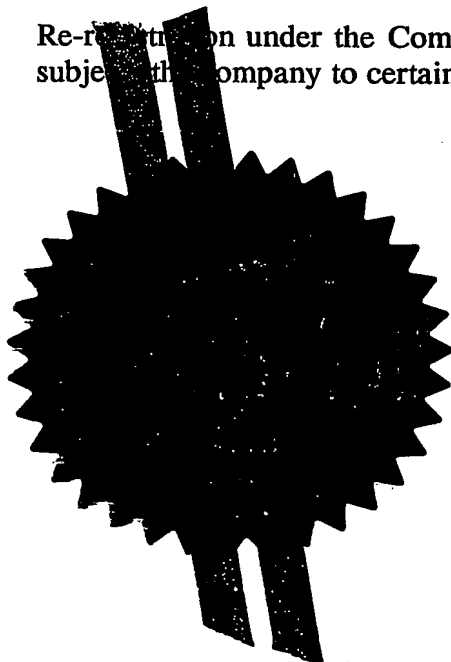


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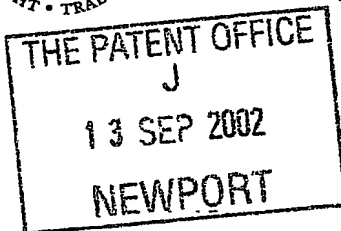
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1/77
PSEP02 E748008-1 D01091
P01/7700 0.00/0221228.0

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1. Your reference

AA 1599 GB

2. Patent application number

(The F

0221228.0

13 SEP 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

JOHNSON MATTHEY PUBLIC LIMITED COMPANY
2-4 COCKSPUR STREET
TRAFALGAR SQUARE
LONDON SW1 Y 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

53 6268007

4. Title of the invention

PROCESS FOR TREATING DIESEL EXHAUST GAS

5. Name of your agent (if you have one)

ANDREW DOMINIC NUNN

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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Country

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Number of earlier application

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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

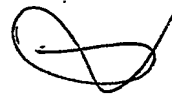
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- a) any applicant named in part 3 is not an inventor, or
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Description	6
Claim(s)	4
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11. I/We request the grant of a patent on the basis of this application.

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PROCESS FOR TREATING DIESEL EXHAUST GAS

The present invention relates to a process for treating exhaust gases from a low-temperature combustion diesel engine, especially when such exhaust gases include unsaturated hydrocarbons.

Conventional diesel engines produce less gaseous hydrocarbon (HC) and carbon monoxide (CO) than gasoline engines and it is possible to meet present legislated limits for these components using a Pt-based diesel oxidation catalyst (DOC). Diesel NO_x emissions are presently controlled by engine management, such as exhaust gas recirculation (EGR). As a consequence, however, diesel particulate matter (PM) emissions, including volatile and soluble organic fractions (VOF and SOF) are increased. The DOC is used to treat VOF and SOF in order to meet legislated limits for PM.

Two ways of reducing diesel emissions, which can be used in addition to exhaust gas aftertreatment, are engine management and engine design. More recently, new diesel engines have been developed which use a range of engine management techniques to lower the combustion temperature. One such technique is to provide means for substantially pre-mixing the air-fuel charge.

An advantage of these techniques is that they can reduce NO_x and PM emissions, without significantly increasing fuel consumption. An embodiment of the new generation of diesel engines which employs these techniques is known as a Homogeneous Charge Compression Ignition (HCCI) engine. Characteristics of an HCCI engine include homogeneous fuel charge for external or internal mixture formation by variable valve timing, increased swirl ratio, injection rate control (multiple injection) and adapted spray configuration; high dilution rate for a moderate burn rate; low NO_x by charge dilution and low combustion temperature; and low soot by long time for mixture preparation and, consequently, homogenisation. All relative terms are compared to a normal direct injection diesel engine

Another embodiment is known as the Dilution Controlled Combustion System (DCCS), for example Toyota's Smoke-less Rich Combustion concept. Characteristics of DCCS include conventional direct injection; extremely high dilution rate to lower combustion temperature below soot formation threshold by increasing ignition lag, increase in swirl ratio, variable valve

timing and injection rate control (multiple injection); low NO_x and soot by very high charge dilution rate and extremely low combustion temperature; and very high EGR rate. All relative terms are compared to a normal direct injection diesel engine

5 We have investigated the emissions of a vehicle including an embodiment of the new generation of diesel engines, such as DCCS and HCCI diesel engines, and have found that, despite the improvements in reduced NO_x and PM, they can produce high levels of CO and HC relative to a conventional direct injection diesel engine. Such CO and HC emissions can be characterised by an exhaust gas composition of >2000ppm carbon monoxide (CO) and >500ppm
0 C_1 unburnt hydrocarbon (HC) below 250°C during normal operating conditions

Furthermore, we believe that unsaturated hydrocarbons may result from the incomplete combustion of the diesel, examples of which are ethylene, propylene, aromatics and polyaromatics. Release of certain unsaturated HCs is undesirable for environmental and health
5 reasons.

We have now identified a family of catalysts that are particularly effective in converting relatively high levels of CO and HC at temperatures below 250°C . Indications are that such catalysts can also convert unsaturated HCs at such temperatures.

0 According to one aspect, the invention provides a process of treating an exhaust gas from a diesel engine, which exhaust gas comprises >2000ppm carbon monoxide (CO) and >500ppm C_1 unburnt hydrocarbon (HC) below 250°C during normal operating conditions measured at the exhaust manifold, which process comprising contacting the exhaust gas with a catalyst
5 comprising at least one supported Platinum Group Metal (PGM) and at least one base metal promoter, wherein the at least one PGM is palladium (Pd) and wherein the atom amount of Pd present is in the majority over all other PGMs present.

According to a further aspect, the invention provides a diesel engine producing an
10 exhaust gas comprising >2000ppm carbon monoxide (CO) and >500ppm C_1 unburnt hydrocarbon (HC) below 250°C during normal operating conditions measured at the exhaust manifold, which engine comprising an exhaust system comprising a catalytic converter, which catalytic converter comprising at least one supported Platinum Group Metal (PGM) and at least

one base metal promoter, wherein the at least one PGM is palladium (Pd) and wherein the atom amount of Pd present is in the majority over all other PGMs present.

Such engines can be controlled, using engine management techniques operated by engine control means e.g. including a CPU and suitable pre-programming, to combust a substantially pre-mixed air-fuel charge.

Two embodiments of engines according to the invention fitted to commercially available vehicles are a homogeneous charge compression ignition (HCCI) diesel engine and a Dilution Controlled Combustion System (DCCS) diesel engine.

We have found that the promoted and supported Pd catalytic component of the catalytic converter according to the invention is at least of zero order kinetics for CO, i.e. the rate of reaction stays the same regardless of the CO concentration. We have also found that for certain of the Pd catalytic components we have identified the rate of reaction is first order for CO, i.e. the more CO, the faster the rate of reaction. By contrast, a widely used PGM in DOCs, platinum (Pt), can be negative order in CO, i.e. the more CO, the lower the reaction rate.

The realisation of the kinetics of promoted and supported Pd catalytic components to the CO reaction has led us to consider uses for the exotherm produced. One such use is to increase the rate of a downstream process step, as described in greater detail hereinbelow.

In its most basic embodiment, we see the sole PGM in the catalytic converter for use in the present invention can be Pd. However, depending on the exhaust gas composition produced by the engine, it can be useful to include one or more non-Pd PGMs in the catalytic converter, subject to the proviso that the atom amount of Pd present is in the majority over all other PGMs present and in preferred embodiment, the non-Pd PGM comprises platinum (Pt). Pt can be particularly useful for oxidising saturated HCs, and is, of course, used as a major component of conventional DOCs for treating SOF.

The at least one base metal promoter for the Pd catalytic component can be a basic metal element or a basic metal compound or any mixture of any two or more thereof. Illustrative examples of basic metals are alkaline earth metals, such as barium, magnesium, calcium or

strontium, or a lanthanide metal, e.g. cerium or lanthanum, or any mixture or mixed oxide of any two or more thereof.

..... In one embodiment, the basic metal compound is ceria, and the Pd is supported on
5 particulate ceria, i.e. the particulate ceria serves as the Pd support and promoter.

Alternatively, the support for the or each PGM can be any conventional support known in the art such as alumina, silica-alumina, titania, zirconia, a zeolite or a mixture or mixed oxide of any two or more thereof, and can be doped, as conventional in the art, with a basic metal or basic
10 metal compound. Non-limiting examples of the basic metal dopant are zirconium, lanthanum, alumina, yttrium, praseodymium, cerium, barium and neodymium. The support can be, for example, lanthanum-stabilised alumina, or zirconium-doped ceria.

The catalytic converter can comprise a conventional substrate, such as a ceramic, e.g.
15 cordierite, or metal, e.g. FecralloyTM, honeycomb. Where the sole PGM present is Pd, a single substrate can be coated with a washcoat including the supported Pd and the at least one base metal promoter. However, where the catalytic converter for use in the present invention includes at least one non-Pd PGM, we envisage that the catalytic converter can take one of several forms. In one embodiment, comprising a single substrate, the supported Pd and the at least one base
20 metal promoter are coated on an upstream part of the substrate and the at least one supported non-Pd PGM is coated on a downstream part thereof. In an alternative embodiment, also comprising a single substrate, the catalytic converter comprises a substrate comprising a first layer comprising the at least one supported non-Pd PGM and a second layer overlying the first layer, which second layer comprising the supported Pd and the at least one base metal promoter.
25 A third embodiment also comprising a single substrate, the substrate is coated with a single washcoat layer, which layer comprising the supported Pd, the at least one base metal promoter and at least one supported non-Pd PGM wherein each PGM is supported on a separate and distinct particulate support material. In an alternative embodiment, the catalytic converter comprises a first substrate comprising the supported Pd and the at least one base metal promoter
30 and a second substrate comprising the at least one supported non-Pd PGM, which second substrate is disposed downstream of the first substrate.

..... In the new generation of diesel engine-installed vehicles, the engines may be controlled to operate in a mode generating low temperature exhaust gases, such as combustion of a

substantially pre-mixed air-fuel charge, over the entire engine load-speed map. However, we envisage that at high loads, the engine control means switches the engine to more conventional diesel combustion as is used in direct injection diesel engines. During such periods of "direct injection" running, levels of NO_x and PM can require treatment in order for the vehicle as a whole to meet the relevant emission legislation.

According to this aspect, the invention provides a diesel engine according to the invention, having a first running condition wherein the engine is configured to run in a mode characterised by the amount of CO and HC produced in the defined temperature range, and a second condition wherein the engine is configured to run in a conventional direct injection diesel engine mode. Control of the first and second running conditions can be effected by the engine control means associated with the engine.

Methods of treating levels of NO_x and PM generated by conventional diesel engines are known and include: a particulate filter downstream of a catalytic converter for oxidising NO to O_2 whereby PM trapped on the filter is combusted in the NO_2 at temperatures of up to 400°C ; a NO_x trap; a catalyst for catalysing the selective catalytic reduction (SCR) of NO_x with at least one NO_x specific reductant, such as a nitrogenous compound, such as a nitrogen hydride, ammonia, an ammonia precursor, e.g. urea, and hydrazine; or a catalyst for catalysing the reduction of NO_x with at least one non-selective reductant, such as H_2 or at least one hydrocarbon. However, where the rate of such methods of treating NO_x and PM are low at the exhaust gas temperatures developed in the first mode, when the switch to second-mode running is effected by the engine control means, the downstream catalysts can be below their effective temperature for treating them.

A benefit of the invention, where downstream treatment of NO_x and/or PM is required, is that the CO exotherm developed over the can be used to raise the temperature of the downstream catalysts, thereby improving the overall conversion in the system. CO content of the exhaust gas in the second mode can be modulated according to exotherm requirement by suitable engine control using methods known in the art.

The catalysts for treating NO_x and/or PM can be any conventional composition known in the art. For example, the NO_x trap can comprise a NO_x absorber, which can comprise an alkali metal compound or an alkaline earth metal compound. Additionally, the NO_x trap can include at

least one PGM, which can be selected from the group consisting of Pt, Pd and Rh, preferable and preferably a combination of Pt and Rh.

5 The SCR catalyst can be Pt-based, e.g. Pt on alumina; vanadium-based, e.g. V_2O_5/TiO_2 ; or a zeolite, e.g. ZSM-5, mordenite, gamma-zeolite or beta-zeolite. The zeolite can comprise at least one metal selected from the group consisting of Cu, Ce, Fe and Pt, which metal can be ion-exchanged or impregnated on the zeolite.

10 The particulate filter can be catalysed, e.g. by at least one of a NO oxidation catalyst, a NO_x absorber, an O_2 combustion catalyst or a catalyst for catalysing the SCR of NO_x .

Where the diesel engine according to the invention includes an exhaust gas recirculation valve and a circuit to recirculate a selected portion of the exhaust gas to the engine air intake, desirably the exhaust gas is cooled prior to mixing with the engine intake air.

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According to a further aspect, the invention provides a vehicle including a diesel engine according to the invention. The vehicle can be, for example, a light duty diesel vehicle as defined by the relevant legislation.

CLAIMS:

1. A process of treating an exhaust gas from a diesel engine, which exhaust gas comprises
5 >2000ppm carbon monoxide (CO) and >500ppm C₁ unburnt hydrocarbon (HC) below 250°C
during normal operating conditions measured at the exhaust manifold, which process
comprising contacting the exhaust gas with a catalyst comprising at least one supported
Platinum Group Metal (PGM) and at least one base metal promoter, wherein the at least one
PGM is palladium (Pd) and wherein the atom amount of Pd present is in the majority over all
other PGMs present.
- 10 2. A process according to claim 1, wherein the PGM comprises also platinum (Pt).
3. A process according to claim 1 or 2, wherein the exotherm produced over the catalyst is used
to increase the rate of a downstream process step.
- 15 4. A process according to claim 3, wherein the downstream process step comprises NO_x
adsorption, NO_x desorption, particulate matter combustion in NO₂ or O₂, NO_x reduction
using a NO_x specific reductant or NO_x reduction using a non-selective reductant, such as
hydrogen (H₂) or at least one hydrocarbon.
- 20 5. A process according to any preceding claim, wherein the diesel engine combusts a
substantially pre-mixed air-fuel charge.
6. A process according to any preceding claim, wherein the diesel engine is a homogeneous
25 charge compression ignition (HCCI).
7. A diesel engine producing an exhaust gas comprising >2000ppm carbon monoxide (CO) and
>500ppm C₁ unburnt hydrocarbon (HC) below 250°C during normal operating conditions
measured at the exhaust manifold, which engine comprising an exhaust system comprising a
30 catalytic converter, which catalytic converter comprising at least one supported Platinum
Group Metal (PGM) and at least one base metal promoter, wherein the at least one PGM is
palladium (Pd) and wherein the atom amount of Pd present is in the majority over all other
PGMs present.

8. A diesel engine according to claim 7, wherein at least one supported PGM comprises also platinum.
9. A diesel engine according to claim 7 or 8, wherein the base metal promoter is a basic metal
5 element or a basic metal compound or any mixture of any two or more thereof.
10. A diesel engine according to claim 9, wherein the basic metal is an alkaline earth metal or a lanthanide metal or any mixture or mixed oxide of any two or more thereof.
- 10 11. A diesel engine according to claim 9, wherein the alkaline earth metal is barium, magnesium, calcium, strontium or any mixture or mixed oxide of any two or more thereof.
12. A diesel engine according to claim 9, wherein the lanthanide metal is cerium or lanthanum.
- 15 13. A diesel engine according to any of claims 7 to 12, wherein the or each PGM support is alumina, silica-alumina, ceria, titania, zirconia, a zeolite or a mixture or mixed oxide of any two or more thereof.
14. A diesel engine according to claim 13, wherein the support is doped with a basic metal or
20 basic metal compound.
15. A diesel engine according to claim 14, wherein the basic metal or basic metal compound is one or more of zirconium, cerium, lanthanum, alumina, yttrium, praseodymium, barium and neodymium.
- 15 16. A diesel engine according to claim 13, 14 or 15, wherein the support comprises lanthanum stabilised alumina.
17. A diesel engine according to claim 13, 14 or 15, wherein the support comprises zirconium-
30 doped ceria.
18. A diesel engine according to any of claims 7 to 17, wherein the catalytic converter comprises at least one substrate.

19. A diesel engine according to claim 18, wherein the catalytic converter comprises a first substrate comprising the supported Pd and the at least one base metal promoter and a second substrate comprising the at least one supported non-Pd PGM, which second substrate is disposed downstream of the first substrate.

5

20. A diesel engine according to any of claims 8 to 18, wherein the catalytic converter comprises a substrate comprising the supported Pd and the at least one base metal promoter on an upstream part of the substrate and the at least one supported non-Pd PGM on a downstream part thereof.

10

21. A diesel engine according to any of claims 8 to 18, wherein the catalytic converter comprises a substrate comprising a first layer comprising the at least one supported non-Pd PGM and a second layer overlying the first layer, which second layer comprising the supported Pd and the at least one base metal promoter.

15

22. A diesel engine according to any of claims 8 to 18, wherein the catalytic converter comprises a substrate coated with a single washcoat layer, which layer comprising the supported Pd, the at least one base metal promoter and the at least one supported non-Pd PGM, wherein each PGM is supported on a separate and distinct particulate support material.

20

23. A diesel engine according to any of claims 7 to 22, having a first running condition wherein the engine is configured to run in a mode which produces the defined levels of CO and HC in the defined temperature range, and a second condition wherein the engine is configured to run in a conventional direct injection diesel engine mode.

25

24. A diesel engine according to claim 23, wherein the engine switches to the second condition during high engine load.

25. A diesel engine according to claim 23 or 24, wherein the first and second running conditions are controlled by an engine control means.

30

26. A diesel engine according to claim 23, 24 or 25, wherein the exhaust system comprises a NOx trap downstream of the catalytic converter.

27. A diesel engine according to claim 23, 24 or 25, wherein the exhaust system comprises a catalyst for catalysing the selective catalytic reduction (SCR) of NO_x with at least one NO_x specific reductant.
- 5 28. A diesel engine according to claim 23, 24 or 25, wherein the exhaust system comprises a catalyst for catalysing the reduction of NO_x with at least one non-selective reductant, such as H_2 or at least one hydrocarbon.
- 10 29. A diesel engine according to claim 23, 24 or 25, wherein the exhaust system comprises an optionally catalysed particulate filter downstream of the catalytic converter.
30. A diesel engine according to any of claims 7 to 29, including an exhaust gas recirculation valve and circuit to recirculate a selected portion of the exhaust gas to the engine air intake.
- 15 31. A diesel engine according to claim 30, wherein the recirculated exhaust gas is cooled prior to mixing with the engine intake air.
32. A diesel engine according to any of claims 7 to 31 which combusts a substantially pre-mixed air-fuel charge.
- 20 33. A diesel engine according to any of claims 7 to 32, wherein it is a homogeneous charge compression ignition (HCCI) diesel engine or a Dilution Controlled Combustion System (DCCS) diesel engine.
- 5 34. A vehicle including a diesel engine according to any of claims 7 to 33.
35. A light duty diesel vehicle according to claim 34.
36. A diesel engine substantially as described herein.
- 0 37. A process of treating an exhaust gas from a diesel engine substantially is described herein with reference to the accompanying Example.

PCT Application
GB0304006

